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CHROMOPHORE PROPERTIES OF HIGH BRIGHTNESS PULPS

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ABSTRACT

The production of high brightness pulps remains one of the principal requirements for many high–value paper products. The need to accomplish this task under the recently proposed cluster rules makes this an especially challenging problem for softwood kraft pulps. Recently, our research group has begun to examine the chemical constituents of kraft pulps that may contribute to a brightness ceiling. As a preliminary study in this field we have examined the potential contribution of *ortho*– and *para*–quinone structures to brightness development during multistage bleaching. Employing literature methods, we have found a relationship between the quinone content after the first alkaline extraction stage and the final brightness values of a kraft pulp. The fate of quinones was explored using a D(E*)DED (E* = E, EAr, EO, EP, and EOP) bleaching sequence with a softwood kraft pulp.

INTRODUCTION

Chemical pulp bleaching involves both brightening and delignification reactions. Delignification can be conveniently studied by the well established measures of kappa number or Klason lignin content. Kappa number is a measure of the ease of oxidation of a pulp and has been correlated with Klason lignin content of chemical pulps [1]. Recent lignin and carbohydrate model compound studies by Li and Gellerstedt have begun to reveal the chemical significance of the kappa number test [2].

McDonough studied the fundamental parameters influencing brightness development during $D_0(E+O)D_1ED_2$ bleaching of softwood kraft pulps [3]. Significantly, the kappa number of unbleached pulp was found to influence brightness response in the D_2 stage. Also, brightness ceilings were higher for modified versus conventional pulps and for pulps with lower unbleached kappa number. Clearly, chemical structures, as quantified by the kappa test, can have an influence that carries throughout the multistage bleaching process.

Pulp brightness is defined as the diffuse reflectance of visible blue light (central wavelength 457 nm) from an "infinite" thickness stack of paper sheets [4]. The brightening process is very important during chemical pulp bleaching and occurs concurrently with delignification. Brightening and delignification reactions both reduce the quantity of chromophoric (colored) structures in the pulp so the resulting paper reflects more light.

The brightening process is difficult to study because of the scarcity of specific methods to probe the nature and quantity of lignin chromophores. Ultraviolet and visible spectroscopy have been used to study chromophore removal during bleaching but precise structural information is difficult to derive from this technique. Also, studies of the brightening process are further complicated by the fact that the exact chemical nature of colored structures in pulp is not known with certainty. Hence, there is a need to understand the fundamental chemistry of brightening.

Quinone Chromophores

The color of chemical and mechanical pulps my arise from structures such as: catechol–metal complexes [5-7], quinone methides [5], stilbenes [5, 8], *ortho*– and *para*–quinones (Figure 1) [5, 6, 9-11]. In particular, quinones have been widely acknowledged to be important chromophores in lignocellulosic materials and they may have a major impact on the brightness of chemical pulps [9, 12].

Ortho -Quinone
(1,2-Benzoquinone)

Para -Quinone
(1,4-Benzoquinone)

Figure 1. General Structure of *Ortho*– and *Para*–Quinones.

In previous studies, we presented trimethylphosphite derivatization as a useful technique for both detection and quantification of the *ortho*– and *para*–quinone structures in kraft residual lignin [13, 14]. Trimethylphosphite derivatization was originally developed to study *ortho*–quinone structures in mechanical pulps [15-19]. Our research group has modified the literature procedure such that the combined *ortho*– and *para*–quinone content in isolated lignin samples can be quantified. The technique relies on the ability of trimethylphosphite to form adducts specifically with *ortho*– and *para*–quinone structures. The "tagged" quinone structures are then quantified with ^{31}P-NMR spectroscopy.

Lignin quinone structures are important because they are strongly colored. Also, commercially important bleaching agents are known to have reaction pathways involving both formation and destruction of quinone structures. Figure 2 illustrates the formation of a *para*–quinone lignin structure. During alkaline oxygen bleaching, *para*–quinone lignin structures may be formed *via* a Dakin reaction involving side–chain elimination at the C_1 position (Figure 2) [20]. *Ortho*– and *para*–quinone structures may also be formed during chlorine dioxide bleaching from phenolic and non–phenolic lignin structures [21-25]. The ability of chlorine dioxide to form lignin quinone structures has recently been studied by our research group [13, 14]. Furthermore, the brightening ability of hydrogen peroxide may be partially explained by the specific destruction of conjugated carbonyl structures, such as quinones, by the hydroperoxide anion [26-28].

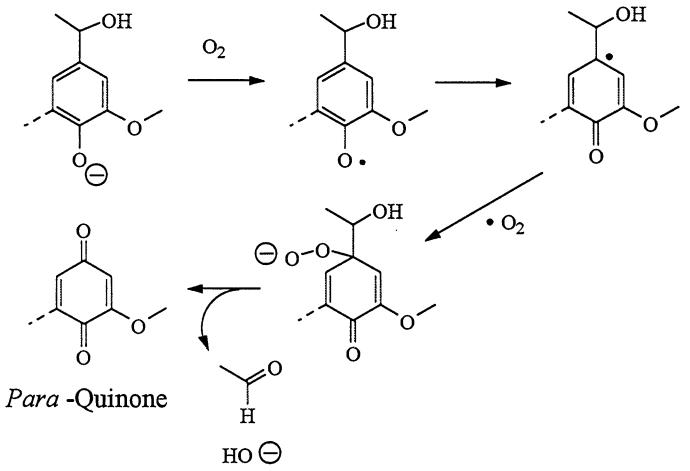

Figure 2. Alkaline Oxygen Reactions of Lignin Leading to the Formation of Quinone Chromophores.

One goal of comparing bleaching response with lignin structural changes is to suggest more efficient use of bleaching chemicals. Potentially, multistage bleaching processes can be better controlled by understanding the chemical modifications that occur as lignin is removed and the pulp is brightened. Specifically, this study attempts to contribute to bleaching process improvement by understanding the impact quinone chromophores have on brightness development during chemical pulp bleaching.

EXPERIMENTAL

Chemicals

All chemicals were commercially purchased and used as received except for 1,4–dioxane, which was purified by distillation over sodium borohydride.

Furnish

All pulps were prepared from a single loblolly pine (*Pinus taeda*) tree grown in Southeastern USA. The tree was debarked, chipped, and screened. On average, chip thickness varied between 2 and 8 mm. The chips were cooked under conventional kraft conditions to give a brownstock of kappa number 30.5.

Chlorine Dioxide Bleaching

D_0 stage pulp was prepared from brownstock under the following conditions: 2.3% ClO_2 charge, 10% consistency, 45°C, final pH = 2.0, and 45–minute reaction. The D_0 pulp was then washed with water; the viscosity was found to be 26.4 cP and the kappa number was 14.6. A portion of the D_0 pulp was alkaline extracted in a series of experiments and further bleached by application of a DED sequence. Bleached pulp was washed and characterized, as previously described [13], by kappa number (TAPPI 236 om–85), and Klason lignin content (TAPPI 222 om–88).

Alkaline Extraction

A series of alkaline extracted pulps was prepared from the chlorine dioxide (D_0) delignified pulp. In a peg mixer, the following basic alkaline extraction stage conditions were used: 10% consistency, 70°C, final pH > 10.5, and 75–minute reaction. Specific details of the alkaline extraction stage conditions are given in Table 1.

Table 1. Oxidative Alkaline Extraction Stage Conditions

Stage	NaOH Charge	Oxidative Reinforcement
E	2.0%	Ambient atmospheric pressure Air
EO	2.5%	Oxygen applied at 0.41 MPa (60 psig), decreased by 83 kPa (12 psig) per 5 minutes
EP	2.5%	0.5% Hydrogen peroxide
EOP	2.5%	0.5% Hydrogen peroxide; Oxygen applied at 0.41 MPa (60 psig) then decreased by 83 kPa (12 psig) per 5 minutes
EAr	2.0%	Air purged; Argon applied at 69 kPa (10 psig)

D_1 and D_2 Bleaching

The alkaline extracted pulps were further bleached with a D_1ED_2 sequence. The following D_1 conditions were used: 0.75% ClO_2 charge, 10% consistency, 70°C, and 3–hour reaction. Second alkaline extraction stage conditions were as follows: 1.0% NaOH charge, 10% consistency, 70°C, and 60–minute reaction. Washed E_2 stage pulps were bleached in a D_2 stage and the brightness ceiling was determined (at a maximum of 0.8% ClO_2 charge).

Residual Lignin Isolation

Residual lignin was isolated from the pulps by a mild acidic 1,4–dioxane hydrolysis procedure modified from the literature [29-32]. In brief, lignin was extracted from the pulp with 90% 1,4–dioxane/0.1 N HCl (v/v) solution (8% consistency) by refluxing for 2 hours under an argon atmosphere. The mixture was then filtered, concentrated, and purified by precipitation. Purified lignin was freeze–dried and analyzed by ^{1}H– and ^{31}P–NMR spectroscopy.

Lignin Quinone Quantification

The combined *ortho*– and *para*–quinone contents of isolated lignins were determined by ^{31}P–NMR spectroscopy after trimethylphosphite derivatization [13, 14]. Dry residual lignin (30 mg) was treated with 500 μL 50% trimethylphosphite/DMSO (v/v) under argon at room temperature. After seven days, excess trimethylphosphite

was removed by vacuum at 40°C for 3 hours. Treated lignins were dissolved in 400 μL DMSO–D_6, containing tri–*meta*–tolyl–phosphate (2.5 mg/mL) and chromium acetylacetonate (1.0 mg/mL). Then 5 μL water (0.3 mmol per 30 mg lignin) was added to the sample and after 12 hours, the ^{31}P–NMR spectrum was acquired with a Bruker 400 MHz NMR spectrometer.

Quantitative ^{31}P–NMR spectra were acquired at 305°K using a 90° pulse, a 5–second pulse delay, and inverse–gated broad–band proton decoupling. For each spectrum 1000–3000 scans were collected. The internal standard, tri–*meta*–tolyl–phosphate (-16.3 ppm vs. 85% H_3PO_4), was used both for quantification and as a shift reference. Quantification of lignin quinone content was achieved by integrating the areas of the internal standard and the quinone adduct resonance at -2.5 ppm [13, 14].

Functional Group Quantification

Lignin functional groups were determined by ^{1}H–NMR spectroscopy using the method of Li and Lundquist [33]. Lignin samples (20 mg) were dissolved in anhydrous DMSO–D_6 containing sodium 3–trimethylsilyl–propionate–2,2,3,3–D_4 as an internal standard. Quantitative ^{1}H–NMR spectra were acquired with a Bruker 400 MHz NMR spectrometer using a 90° pulse and a 25–second pulse delay. For each spectrum 200 scans were collected.

RESULTS AND DISCUSSION

Residual Lignin Quinone Contents

From initial ^{31}P-NMR studies, the combined *ortho*– and *para*–quinone content of brownstock residual lignin was found to be 0.088 mmol quinone/g lignin (≡ 1.6 quinones per 100 C_9) and this value was compares favorably with literature values for softwood kraft lignins: Furman and Lonsky found 3 quinones per 100 C_9 using reductive acetylation [34] and Iiyama and Nakano found 3-4 quinones per 100 C_9 by using visible absorbance [35].

Quinone contents for a series of alkaline extraction treatments and D_1 stage residual lignins are given in Figure 3. Generally, the increased application of oxidative reinforcement during alkaline extraction results in a lower quinone content. For example, the quinone content of alkaline extraction stage residual lignin with air excluded, D(EAr), is 190% more than when both hydrogen peroxide and pressurized oxygen, D(EOP), are applied. As shown in Figure 3, the order of increasing quinone content is as follows: D(EP) < D(EOP) < D(EO) < D(EAr) < DE. As has been previously noted [13], hydrogen peroxide in the alkaline extraction stage, D(EP) or D(EOP), results in a dramatic decrease in quinone content because of the specific reaction of hydroperoxide anion with quinone structures [26-28].

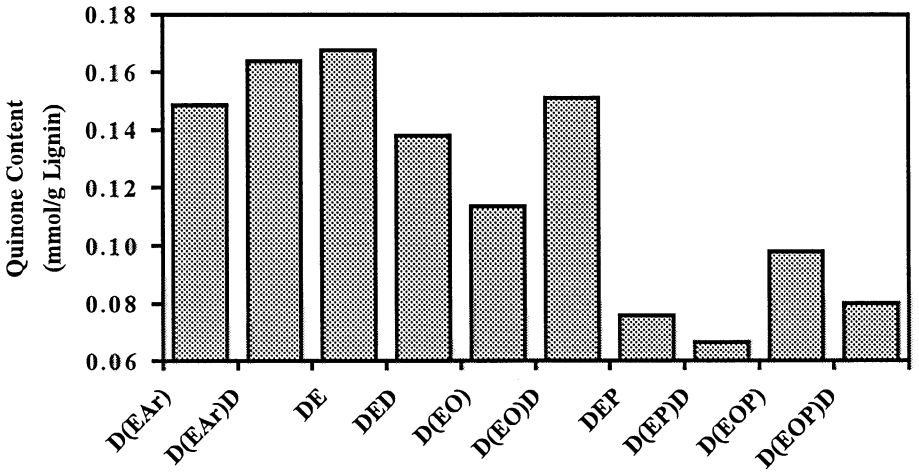

Figure 3. Quinone Contents of E Stage and D_1 Stage Residual Lignins

The quinone content, on a mmol/g lignin basis, is generally lower at the D_1 stage than at the alkaline extraction stage. Two notable exceptions are alkaline extraction with air excluded, D(EAr), and with applied pressurized oxygen, D(EO). Both D(EAr)D and D(EO)D residual lignins displayed a greater quinone content at the D_1 stage than at the previous alkaline extraction stage.

During this study it was noted that E_1 stage Klason lignin content for D(EO) residual lignin was 4.4 g/kg pulp OD and similar in value to that for the D(EP) residual lignin (4.5 g/kg pulp OD). In contrast the E_1 quinone contents for the same residual lignins were vastly different with 0.114 mmol quinone/g lignin for D(EO) residual lignin versus 0.076 mmol quinone/g lignin for D(EP) residual lignin (Figure 3). The E_1 quinone content values are consistent with the higher D_1 and D_2 brightness achievable for the D(EP)DED over the D(EO)DED sequence.

The direct precursors for quinone structures can be envisioned to be phenolic, aromatic, and/or methoxyl groups. Shown in Figure 4 are the unsubstituted phenolic, C_5–substituted phenolic, aromatic, and methoxyl proton contents for the series of alkaline extraction stage residual lignins. Comparing Figure 3 with Figure 4, correlation between precursor functional groups and quinone contents is not readily observed. The difficulty encountered may suggest that a specific subset of these functional groups – such as catechols – is more amiable for conversion to quinones. Alternatively, conversion may be dependent on the oxidant applied, application conditions, and/or presence of other lignin functional groups not studied.

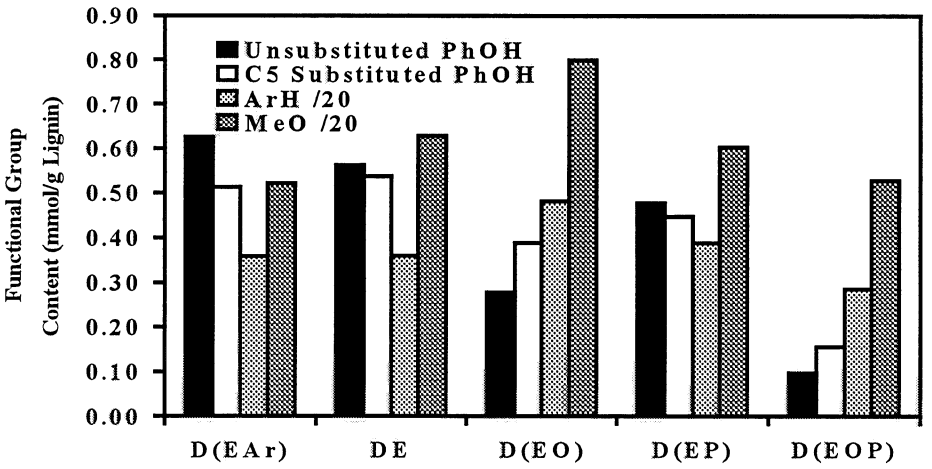

Figure 4. Functional Group Content of E_1 Stage Residual Lignins

In Figure 5 the quinone content data is plotted as "apparent" quinone concentration, that is, a measure of the concentration of the quinone chromophores in the pulp system. To estimate the quantity of lignin in the pulp, Klason lignin content was used. If residual lignin quinone content (mmol/g lignin) is multiplied by the pulp Klason lignin content (g/kg pulp OD), an estimation of quinone chromophore content in the pulp is derived (mmol/kg pulp OD).

Quinone Content Brightness Correlation

As we presented above, a measure of the "apparent" concentration of quinone chromophores in the bleached pulps can be estimated by multiplying the residual lignin quinone content by the pulp Klason lignin content. If the "apparent" quinone chromophore concentration influences pulp brightness then this chromophore concentration should obey the Kubelka–Munk relationship. The Kubelka–Munk equation (Equation 1) describes brightness (reflectance) of a sheet as a function of light absorbance and scattering.

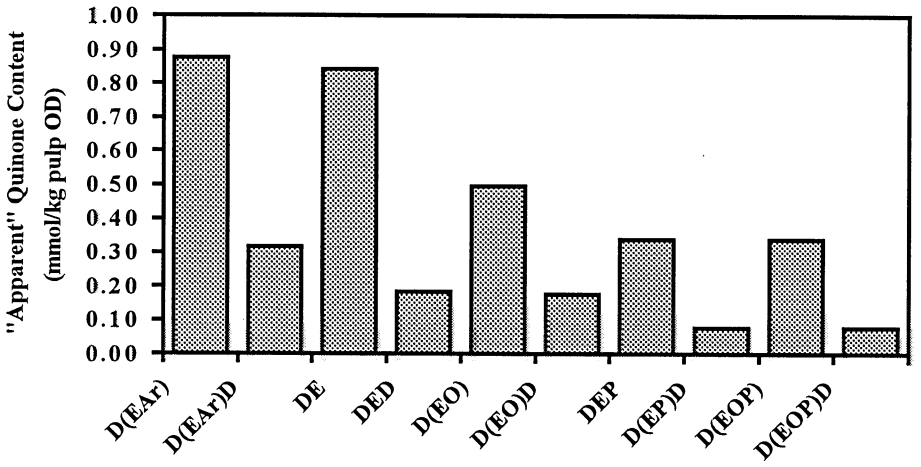

Figure 5. The "Apparent" Quinone Concentration in Bleached Kraft Pulps (E_1 Quinone Content Multiplied by the E_1 Klason Lignin Content)

$$\frac{B}{100} = 1 + \frac{k}{s} - \sqrt{2\left(\frac{k}{s}\right) + \left(\frac{k}{s}\right)^2} \qquad \text{Equation 1}$$

where,
B = brightness (%) {note: $B_{457nm}/100 = R_\infty$= reflectivity of an "infinite" layer of sheets}
k = absorption coefficient
s = scattering coefficient

Generally, modern commercial bleaching has little influence upon the scattering coefficient (s) which is a function of the fiber dimensions and interfiber bonding [4, 36]. For this study, we assumed that altering oxidative reinforcement in the E_1 stage has little influence on D_1 and D_2 scattering coefficients. We also assumed that the absorption coefficient (k) is proportional to the chromophore content (Equation 2 and Equation 3) and that chromophores are evenly distributed throughout the pulp.

From wood, chemical, and mechanical pulp studies, it has been generally assumed that lignin is the major component responsible for light absorption [36-41] although other studies have suggested that the carbohydrate component may also contribute [42, 43]. Given all of the above assumptions, the expected correlation between lignin chromophore content and pulp brightness is described in Equation 4. From Equation 4 it follows that if a given lignin chromophore/structure has a significant impact on pulp brightness then a plot of $1+C-(2C+C^2)^{1/2}$ versus brightness should yield a linear line.

$$\frac{k}{s} = \left(\frac{\phi}{s}\right) \times C \qquad \text{Equation 2}$$

where,
ϕ = proportionality constant, C = chromophore concentration

If s is assumed to be constant then,

$$\frac{k}{s} = \phi_1 \times C \text{ or } \frac{k}{s} \propto C \qquad \text{Equation 3}$$

where,
ϕ_1 = proportionality constant

So,

$$B \propto 1 + C - \sqrt{2(C) + (C)^2} \qquad \text{Equation 4}$$

Table 2 illustrates data derived from plotting various functional group contents and "apparent" contents in pulp against D_1 and D_2 stage brightness values. The R^2 values were calculated for a linear line drawn through the data. Both E_1 stage kappa number and Klason lignin content are correlated with D_1 brightness and the D_2 stage brightness ceiling (Table 2 and Figure 5). These finding are consistent with resulted presented by McDonough who found D_1 and D_2 brightness values are dependent upon unbleached kappa number [3]. This study suggests that, for DE*DED pulps (E* = E, EAr, EO, EP, and EOP), E_1 stage kappa number, E_1 and D_1 Klason lignin contents are all expected to be a good predictors of brightness in both D_1 and D_2 stages.

Table 2. R^2 Values for a Linear Line Fit through Brightness versus $1+C-(2C+C^2)^{1/2}$ for DE*DED Pulps

		R^2	
Entry	Data Used for C [a]	D_1 Brightness	D_2 Brightness
	Klason and Kappa		
1	E_1 Klason Content	0.81	0.78
2	D_1 Klason Content	0.75	0.79
3	E_1 Kappa Number	0.71	0.71
	Quinone Contents		
4	E_1 Quinone Content	0.60	0.76
5	D_1 Quinone Content	0.81	0.84
	"Apparent" Quinone Contents		
6	(E_1 Quinone Content) x (E_1 Klason Content)	0.80	0.93
7	(D_1 Quinone Content) x (E_1 Klason Content)	0.95	0.98
8	(D_1 Quinone Content) x (D_1 Klason Content)	0.90	0.96
9	(D_1 Quinone Content) x (E_1 Kappa Number)	0.96	1.00
10	(E_1 Quinone Content) x (E_1 Kappa Number)	0.78	0.89
	Proton Functional Group Contents		
11	E_1 Aromatic–H Content	0.30	0.13
12	E_1 Methoxyl–H Content	0.05	0.00
13	E_1 Unsubstituted Phenolic–H Content	0.60	0.50
14	E_1 C_5–Substituted Phenolic–H Content	0.67	0.53
	"Apparent" Proton Functional Group Contents		
15	(E_1 Aromatic–H Content) x (E_1 Klason Content)	0.72	0.52
16	(E_1 Methoxyl–H Content) x (E_1 Klason Content)	0.74	0.54
17	(E_1 Unsubstituted Phenolic–H Content) x (E_1 Klason Content)	0.65	0.53
18	(E_1 C_5–Substituted Phenolic–H Content) x (E_1 Klason Content)	0.72	0.58

E* = E, EAr, EO, EP, and EOP

[a] Klason lignin content (g/kg pulp OD); quinone and proton functional group contents (mmol/g lignin); "apparent" quinone and proton functional group contents (mmol/kg pulp OD)

Unsubstituted phenolic, C_5–substituted phenolic, aromatic, and methoxyl proton contents (weight–lignin basis, mmol/g lignin) are not well correlated with D_1 and D_2 brightness values (Table 2). Particularly, it can be noted that the methoxyl proton absolute content displays a very poor correlation with the D_1 or D_2 stage brightness. First alkaline extraction stage "apparent" phenolic proton content is better correlated with D_1 stage brightness values (Table 2 and Figure 6).

Table 2 reveals that both E_1 and D_2 stage lignin quinone contents are correlated with D_1 and D_2 brightness values. "Apparent" D_1 and E_1 quinone contents are also correlated with D_1 and D_2 brightness values (Table 2 and Figure 6). The correlation suggests that quinone structures may be important chromophores that impact on the brightness values for DE*DED pulps (E* = E, EAr, EO, EP, and EOP).

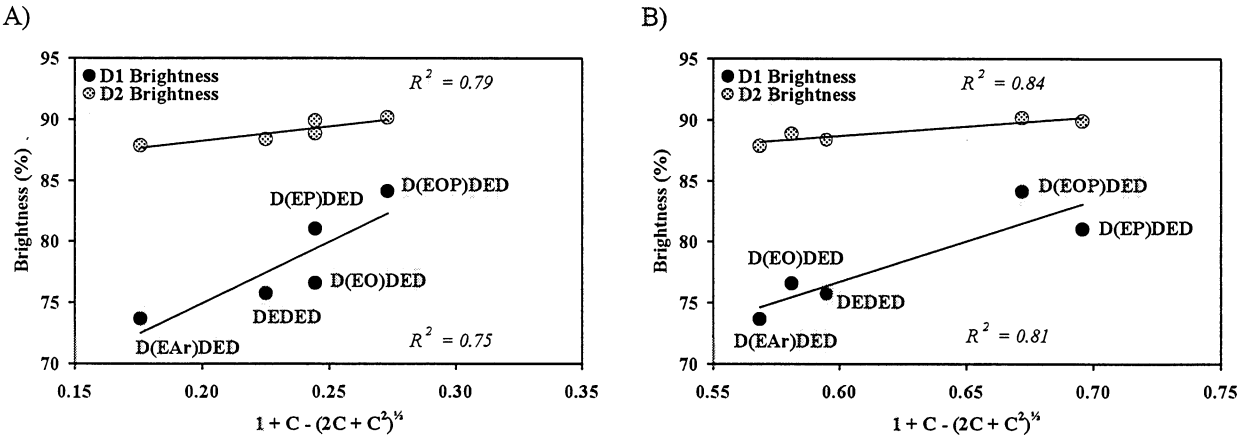

Figure 5.
A) D_1 Klason Lignin Content Correlated with D_1 and D_2 Stage Brightness.
B) D_1 Quinone Content Correlated with D_1 and D_2 Brightness.
{note: $1+C-(2C+C^2)^{1/2}$ is the right–hand side of the proportionality derived from the Kubelka–Munk equation (Equation 4)}

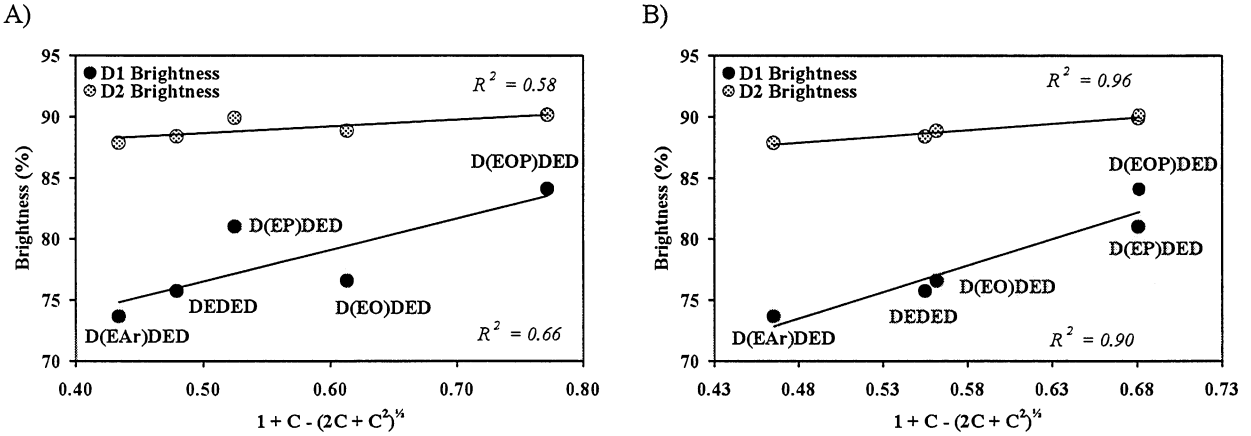

Figure 6.
A) "Apparent" E_1 Unsubstituted Phenolic-H Concentration Correlated with D_1 and D_2 Brightness.
B) "Apparent" D_1 Quinone Concentration Correlated with D_1 and D_2 Brightness.
{note: $1+C-(2C+C^2)^{1/2}$ is the right–hand side of the proportionality derived from the Kubelka–Munk equation (Equation 4)}

CONCLUSIONS

Trimethylphosphite derivatization combined with ^{31}P-NMR spectroscopy is a useful technique for observing changes in the quinone chromophore contents of residual lignins. Further work is in progress exploring the fundamental nature of the technique and applying it to multistage bleaching sequences.

For DE*DED (E* = E, EAr, EO, EP, and EOP) softwood kraft pulp, the "apparent" content (mmol/kg pulp OD) of quinone chromophores was found to be correlated with both D_1 and D_2 brightness values.

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